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## SOLUTION FOR AND METHOD OF CLEANING AND COATING METALLIC SURFACES

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The present invention relates to a method and material for cleaning and coating surfaces of metals such as iron, aluminum, zinc, steel, stainless steel, or the alloys of iron, aluminum and zinc, or metallic surfaces having a preliminarily formed chemical coating thereon. More particularly, this invention relates to an improved material which simultaneously cleans and produces a substantially integral coating on a metallic surface or a chemically coated metallic surface, to thereby render the surface more receptive to paint or the like.

It is well known that the presence of foreign matter such as grease, metal salts, finger prints, etc., on a metallic or chemically coated surface, renders paint applied to that surface subject to blistering and subsequent peeling. It is recognized that some time necessarily elapses between the manufacture of metallic articles having their surfaces chemically treated to avoid corrosion, and the time when that material is fabricated into a desired article and is ready for final surface finishing. During the elapsed time such materials are subjected to handling, as incidences of shipping, warehousing and fabrication, thereby introducing various types of foreign matter to the surfaces of the material. The elimination of such foreign matter is necessary in order to obtain a successful siccative coating thereon.

It is one of the objects of the present invention to provide a solution capable of both cleaning the surface and producing thereon a coating which provides an improved base for paint.

It is a further object of this invention to provide a combined solvent wipe and rinse for chemically coated surfaces or chemically coated and rinsed metal surfaces which improves the adherence of siccative coats applied thereto, and is fast drying and easy of application.

Another object of this invention is to provide a method for applying a combined cleaning and coating solution to the surface of metals or chemically coated metals.

Other objects and advantageous features of the invention will be specifically pointed out or will become apparent upon considering the present disclosure in its entirety.

In accordance with the present invention, it has been found that the aforementioned objectives may be accomplished by applying a solution comprising tertiary butyl alcohol, chromic acid and hydrocarbon solvent to the surfaces of the heretofore mentioned metals or chemically coated metals. The scope of usefulness of this solution may be increased by adding thereto a controlled proportion of water, for it has been found that metallic salts and products of corrosion are more easily removed from the treated surface in the presence of water than in its absence. A properly compounded solution containing these constituents has been found to be effective in removing grease spots, metallic salts, products of corrosion and human finger prints from the surface of the metal so treated and depositing thereon, a thin, uniform

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film of hexavalent chromium which provides an excellent base for siccative coatings.

In preparing the solution of this invention, it will be appreciated that chromic acid is substantially insoluble in solvents capable of dissolving grease, oil, gum and coal tar derivatives such as pitch, bitumen and the like. For the purposes of this invention, such solvents will be hereinafter denominated as hydrocarbon solvents, and the term is intended to include aliphatic hydrocarbons, aromatic hydrocarbons, chlorinated hydrocarbons, cyclic hydrocarbons of the naphthene type and cyclic hydrocarbons of the terpene type and mixtures thereof. Furthermore, chromic acid, known to be a strong oxidizing agent, must be compatible with the other constituents in the solutions, so that it will not be reduced prior to the time of application to the surface to be treated. It is furthermore desirable that the solution contain a blending agent capable of mutually dissolving water and the hydrocarbon solvent thereby rendering chromic acid and water compatible with the hydrocarbon solvent or solvents. For this purpose, tertiary butyl alcohol has been found to be particularly well suited.

Broadly, the composition of this invention may have the following proportions of ingredients:

25	Tertiary butyl alcohol.....	40-90 parts by volume.
	Hydrocarbon solvent.....	10-60 parts by volume.
	Water.....	0 to saturation.

To the above formulation, chromic acid should be added in proportion to produce .025% to 10% chromic acid by weight of the total weight of the formulation. Additionally, it has been found, that water may be present in excess of saturation, and in proportions equal to and exceeding the total volume of hydrocarbon solvent and tertiary butyl alcohol when a dispersion is formed of the water and organic solvents. A preferred formulation from the standpoints of economy, efficiency and breadth of usefulness is:

40	Hydrocarbon solvent....	20-40 parts by volume.
	Tertiary butyl alcohol....	80-60 parts by volume.
	Water.....	1-30 parts by volume.
	Chromic acid.....	.1%-4% by weight of the total solution.

In the above given formulations, the hydrocarbon solvent and the tertiary butyl alcohol, are preferably combined, within the stated limits, to form a total of 100 parts by volume.

Especially beneficial results have been obtained from the use of an aliphatic hydrocarbon solvent having a boiling range of from 180° C. to about 207° C.; a flash point of 143° F., as determined in a Tag closed cup by American Society for Testing Materials methods; an evaporation speed of 58 minutes as compared to an evaporation speed of .6 minute for hexane and 4.5 minutes for light naphtha, commonly known as VM & P naphtha; and a specific gravity of .803. This particular solvent is commercially known as Amsco Solvent #140 and is available from American Mineral Spirits Company. This solvent has a desirably uniform flash point and is especially beneficial because of its slow evaporation speed. It is to be realized, however, that any solvent encompassed by the term "hydrocarbon solvent" which is capable of dissolving grease, oil, or the like and having a boiling range extending from about 50° C. to about 270° C. may be satisfactorily used, such, for example, as light naphtha, high flash VM & P naphtha, naphtholite, special light naphtha or naphthol, mineral spirits, heavy naphtha, high flash mineral spirits, kerosene, benzene, toluene, xylene, "Ring" hydrocarbons containing naph-

HC solvents

range

preferred range

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thenes, cyclic hydrocarbons, gum turpentine, steam distilled wood turpentine and dipentene.

In general, the solutions of this invention may be applied to metallic surfaces or chemically treated non-metallic surfaces by spraying, wiping, brushing or dipping. Most beneficial resistance to subsequent blistering and peeling has been found to result when the deposited film of hexavalent chromium on the treated surface has a weight of between about .003 milligram per square foot to about 10 mgs. per square foot, and even better results are obtained when the coating weight falls within the range of about 1 to 4 mgs. per square foot. It will be clear that the optimum concentration of chromic acid in the solution will vary with the method of application to the surface. For example, in solutions prepared for spraying, the concentration of chromic acid should be substantially lower than in solutions which are to be applied by wiping, since the wiping action tends to remove the greater proportion of the applied chromic acid. After spraying, the excess solution is allowed to drain off and the residual film is formed on the surface by drying either in air or in temperatures between 150° F. to about 350° F. Excess and undesirable quantities of hexavalent chromium may remain on the surface if the concentration of chromic acid is too high in the solution which is applied, for example, concentrations exceeding about 4% by weight of the solution. While the concentration of chromic acid may not, therefore, be predetermined with certainty, it is apparent that the desired concentration may be determined by a few routine tests under actual operating conditions. The same considerations will be seen to apply also in the case of applying the solution to the surface by dipping.

When applying the solution on the surface by wiping, it is only necessary that the entire surface be wiped with a cloth which has been dampened with the solution, and care should be taken that an even coverage is obtained. Air drying or raised temperature drying may be used. After the hexavalent chromium film has dried, the surface is then ready for the immediate application of paint. As used herein, the term "paint" is intended in its broad sense to include varnishes, lacquers, enamels and coating materials always referred to as paints.

Surfaces which are soiled only with grease, oil, gum or the like, may be satisfactorily cleaned with a solution containing no water whatsoever. In those instances, however, in which the surface is also soiled with metallic oxides such as the oxides of zinc or iron or fingerprints, it has been found that the presence of water is necessary. Inasmuch as a solution containing water loses some of its stability or storage ability, water is preferably added to the other constituents just prior to using. Within a reasonable time after admixing with water, the solution will still produce satisfactory results, for example, at any time within about a week after mixing. The presence in the solutions of this invention of tertiary butyl alcohol and hydrocarbon solvents, render them more rapid in evaporation and consequently in the formation of the hexavalent chromium coating on the surface, such that the tendency for build-up of thick hexavalent chromium films at the lower edges of the work piece is appreciably reduced. Furthermore, materials which have been previously chemically coated and additionally rinsed in conventional chromic acid-water solutions are beneficially aided by the method of the present invention by dissolving the usually uneven hexavalent chromium film, and replacing the same with a thin, uniformly distributed hexavalent chromium film, and, of course, simultaneously removing any foreign matter from the surface.

The following examples are given to illustrate the invention, but it is to be understood that these are given only for illustrative purposes and not with the intention of limiting the scope of the invention to the specific proportions, ingredients or other specified conditions set forth therein.

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TABLE 1

No.	Amsco #140, <sup>1</sup> ml.	Tert. Butyl Alcohol, ml.	Chromic Acid, grams	Water, ml.
1	20	80	4	2
2	30	70	2	0
3	50	50	3	20
4	10	90	4	0
5	20	80	.4	.4
6	100	200	.6	400
7	100	200	.6	600

<sup>1</sup> Aliphatic hydrocarbon having a boiling range of from 180° C. to 207° C.

Each of the above solutions was applied, by wiping, to the surfaces of a number of panels of iron, zinc, aluminum, steel, stainless steel, as well as to a number of metallic surfaces which had been coated with a phosphate coating such as zinc phosphate or iron phosphate. After wiping, some of the panels were allowed to dry in air, and others were dried at a temperature of approximately 300° F. for 20 minutes. The panels were then painted by conventional methods. Thereafter, the panels were subjected to conventional salt spray and humidity tests, and excellent results were obtained, that is to say, there was no evidence of blistering or peeling in the humidity tests and creepage of corrosion was exceptionally superior to that which results on panels whose surfaces are dirty, oxidized or contain fingerprints thereon. Somewhat better results were observed with formulations #6 and #7.

A typical formulation having a wide range of general use is as follows:

#### Example 1

Amsco #140	-----ml.	100
Tert. butyl alcohol	-----ml.	200
Chromic acid	-----grams	.6
Water	-----ml.	33

As indicated above, the water is added in this formulation somewhat close to the time of intended use. The other portions of the formulation form a stable transportable solution.

#### Example 2

Heavy naphtha (mineral spirits having a boiling range between about 155° C. and 195° C. and a specific gravity of .786)	-----ml.	50
Tert. butyl alcohol	-----ml.	50
Water	-----ml.	5
Chromic acid	-----grams	2.5

The proportions of heavy naphtha and tertiary butyl alcohol were varied in approximately 10 ml. intervals throughout the range of 40 to 90 ml. of tertiary butyl alcohol, and 10 to 60 ml. of heavy naphtha. The sum of the two ingredients always equalled 100 ml., and the water was varied from 0 to about 30 ml., which approximated saturation at 90 parts tertiary butyl alcohol, and 10 parts heavy naphtha. The chromic acid was varied to produce compositions having a chromic acid content from .025 up to approximately 10%. A plurality of panels were treated in accordance with the procedure set forth under Table 1, and comparable results were obtained in all cases.

The heavy naphtha of Example 3 was substituted for by a number of other hydrocarbon solvents including toluene, xylene, gum turpentine and kerosene. In each instance, grease, oil, finger prints or metallic oxides which were present on the surface of the panels were either removed or neutralized, and the dried coatings of hexavalent chromium proved to be an excellent base for the applied paint coating when tested in the manner indicated under Table 1.

What is claimed is:

1. A method of treating the surface of a metal of the class consisting of iron, aluminum and zinc and the alloys thereof, and chemically coated metallic surfaces which

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comprises applying to the said surface, a solution containing as essential ingredients 40 to 90 parts by volume tertiary butyl alcohol, 10 to 60 parts by volume of a hydrocarbon solvent, up to 30 parts by volume water, and .025% to 10% chromic acid by weight of the total weight of the solution and drying a film of said solution upon the surface.

2. A method of treating the surface of a metal of the class consisting of iron, aluminum and zinc and the alloys thereof, and chemically coated metallic surfaces which comprises applying to the said surface, a dispersion containing as essential ingredients 40 to 90 parts by volume tertiary butyl alcohol, 10 to 60 parts by volume of a hydrocarbon solvent, .025% to 10% chromic acid by weight of the combined weight of tertiary butyl alcohol and hydrocarbon solvent and a proportion of water in excess of that which is soluble in the solution of tertiary butyl alcohol, hydrocarbon solvent and chromic acid, and drying a film of the said dispersion upon the surface.

3. A method in accordance with claim 1, wherein the film dried upon the surface has a weight between about .003 mg. per square foot and about 10 mgs. per square foot.

4. A method in accordance with claim 2 wherein the weight of the film on the said surface is between about .003 mg. per square foot and about 10 mgs. per square foot.

5. A method of treating the surface of a metal of the class consisting of iron, aluminum and zinc and the alloys thereof, and chemically coated metallic surfaces which comprises applying to the said surface a solution containing as essential ingredients tertiary butyl alcohol, a hydrocarbon solvent, and chromic acid, said alcohol being present in an amount of about 40 parts to 90 parts by volume, said solvent being present in an amount of about 10 parts to 60 parts by volume and said chromic acid being present in an amount of about .25% to 10% by weight of the total weight of the solution.

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6. A composition of matter for preparing surfaces of the class consisting of metals and chemically coated metals for receiving a siccative coating consisting essentially of 40 to 90 parts by volume tertiary butyl alcohol, 10 to 60 parts by volume of a hydrocarbon solvent, and .025% to 10% chromic acid by weight of the total solution.

7. A composition of matter for preparing surfaces of the class consisting of metals and chemically coated metals for receiving a siccative coating consisting essentially of 40 to 90 parts by volume tertiary butyl alcohol, 10 to 60 parts by a volume of a hydrocarbon solvent, up to 30 parts by volume water, and .025% to 10% chromic acid by weight of the total solution.

8. A composition of matter for preparing surfaces of the class consisting of metals and chemically coated metals for receiving a siccative coating consisting essentially of 40 to 90 parts by volume tertiary butyl alcohol, 10 to 60 parts by volume of a hydrocarbon solvent, 0.025%–10% chromic acid by weight of the combined weight of tertiary butyl alcohol and hydrocarbon solvent and water in excess of the amount which is soluble in the solution consisting of tertiary butyl alcohol, hydrocarbon solvent and chromic acid.

9. A composition of matter for preparing surfaces of the class consisting of metals and chemically coated metals for receiving a siccative coating consisting of 100 ml. aliphatic hydrocarbons having a boiling range of from 180° C. to 207° C., 200 ml. tertiary butyl alcohol, 33 ml. water and .6 gram chromic acid.

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